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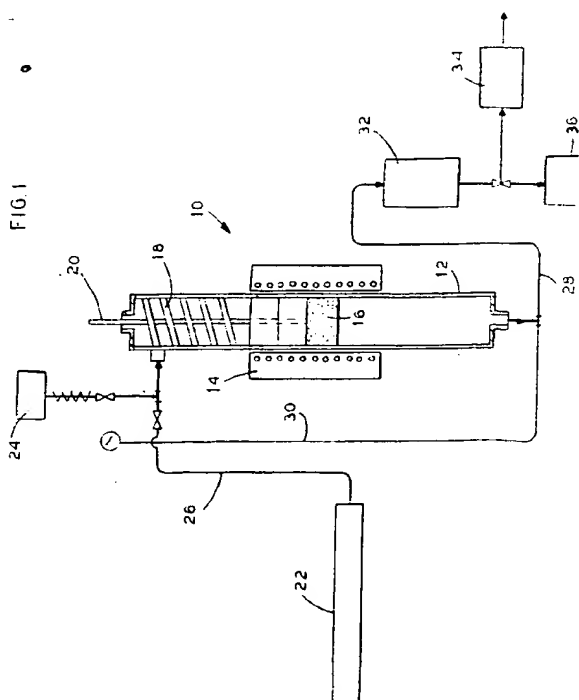
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(54) **Catalytic conversion of internal combustion engine exhaust gases.**

(57) A technique for substantially reducing nitrogen oxide (NO_x) emissions in internal combustion engine exhaust gases. The NO_x laden stream is contacted with a catalytic material supported on a metal plated foam substrate in the presence of a reducing agent. The NO_x is reduced to nitrogen, water and/or carbon, and carbon dioxide.



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TECHNICAL FIELD

The instant invention relates to exhaust gas treatment systems in general and, more particularly, to catalytic techniques for substantially reducing noxious exhaust components generated by diesel engines.

BACKGROUND ART

It has been widely recognized that exhaust emissions from internal combustion engines are directly hazardous to the health of living organisms and to the environment. As a result, diesel engine emissions of nitrogen oxides (NO_x) and particulates from diesel engines, which traditionally have been afforded more lenient treatment than Otto cycle engines, are increasingly being regulated by governmental agencies.

Accordingly, various techniques are under active consideration to reduce noxious emissions emanating from these engines. Concepts include engine modifications and improvements, alternate and reformulated fuels (i.e., hydrogen), and exhaust after treatment devices such as traps, catalyzed traps and catalytic converters.

Unfortunately, engines modified or improved to reduce NO_x emissions usually have increased particulate emissions. On the contrary, methods for reducing particulates generally increase NO_x emissions.

Surveys of the art appear to reflect that most of the work has been concentrated on the reduction of particulate emissions. This avenue of attack includes filter traps, catalytic and fuel additive systems designed to reduce fast ignition temperature and regeneration. On the other hand, work on NO_x reduction from diesel engines has been somewhat limited. It is surmised that this difficult problem has been exacerbated by high oxygen levels in the exhaust stream. With the introduction of new and tighter standards scheduled to become effective in the near future, NO_x reduction in diesel exhausts will require new catalytic systems capable of functioning effectively in high oxygen atmospheres.

Though a number of stationary systems have been successfully commissioned, no similar systems appear to exist in the transportation sector. The catalytic reduction of NO_x by NH_3 (ammonia) over a copper catalyst has been effectively demonstrated where fossil fuels are used to heat boilers, reactors, etc. It is not applicable to vehicles mainly because of the potential hazard posed by the on board storage of NH_3 , and to a lesser extent, because of the effects of low NH_3 vapor pressures on the highly controlled delivery system required to match the rapid variations in NO_x content during operation. In the laboratory, tests suggested that Cu and NH_3 incorporated into zeolite resins may be effective in the catalytic reduction of NO_x . However, its effectiveness as a de NO_x catalyst seemed limited by its durability. Though the influence of diesel fuel-water emulsions (water/fuel ratios ≤ 0.25) on particulates and NO_x is very significant, large increases of carbon monoxide (CO) and condensibles (polynuclear aromatic hydrocarbons [PAH]) make the process unattractive. Relatively small amounts of water in the emulsions give very large reductions in NO_x and particulates.

A recent publication claimed to have electrocatalytically reduced NO_x emissions from vehicles fueled by natural gas. See Marshalla M. Wright, et al, "Solid State Electrochemical Cell for Nitrogen Oxide (NO_x) Reduction" Proc. Intersoc. Energy Convers. Eng. Conf. 27, Volumes 4, pages 4.321-4.325 (1992). The cathodes describe a honeycomb shaped ceramic coated with silver (or silver containing conducting material) in two distinct regions so that a cathode and anode were formed with an applied voltage across the system. Electrocatalytic reduction at the cathode resulted in the NO_x going to N_2 and 2O , as the exhaust gas flowed through the channels. The N_2 continued through the cell while the O ions, dissolved in the solid electrolyte, usually consisting of zirconia (ZrO_2), hafnia (HfO), titania (TiO_2), or the lanthanide oxides, were converted to O_2 at the anode. Although promising, this is very new technology and must yet clear several obstacles before it can be considered viable.

U.S. Patent 5,106,802 discloses a diesel engine catalyst employing a honeycomb structure. A number of catalytic materials including silver are enumerated.

SUMMARY OF THE INVENTION

Accordingly, there is provided a method for substantially reducing objectionable components, particularly NO_x , from exhaust gas streams of internal combustion engines.

The instant invention is particularly applicable to diesel engine exhaust gases having oxygen levels considerably greater than those of an Otto engine operating at or around the stoichiometric burn. The exhaust gases are contacted with a metallic catalyst supported on a sponge-like metallic substrate such as nickel plated polymeric foam to which sufficient reducing agents (HN_3 , urea [HN_2CONH_2], CO, or hydrocarbon fuels [hexane, butane, methane, natural gas, etc.]) are added to catalytically reduce NO_x to N_2 and water or CO_2 .

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an elevation of an embodiment of the invention.

Figure 2 is a schematic diagram of an embodiment of the invention.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Figure 1 depicts a laboratory exhaust gas catalytic converter assembly 10. The converter 10 includes a reactor 12. For testing purposes the reactor 12 is shown disposed within a furnace 14. During engine usage, the high temperature of the exhaust gases would be sufficient to heat the reactor 12.

A metallic catalyst 16, preferably metallic silver, supported by the nickel sponge is disposed within the reactor 12. Heating tape 18 preheats the upstream portion of the reactor 12. This serves to assist in raising the entrance temperature of the gases entering the reactor 12. A thermocouple 20 measures the temperature of the interior reactor 12.

A source of exhaust gas 22 is connected to the reactor 12. A source of water vapor 24 is tapped into an input line 26. The gas exits the reactor 12 through outlet line 28. A by-pass line 30 optionally routes the exhaust gas around the reactor 12 to the outlet line 28.

In order to analyze the composition of the exhaust gas after catalytic treatment, the outlet line 28 leads to a water cooled condenser 32. The condensed gases then flow into a gas analyzer 34 and then out. Alternatively, the gases may be directly routed to a vent 36.

Figure 2 depicts in schematic fashion, a three stage catalytic converter 40 attached to a diesel engine 42. It will be appreciated, however, that the terms stage or zone are merely for discussion. They are not limiting terms.

An exhaust manifold 44 preferably splits the exhaust flow into two pathways 46 and 48 leading to a first zone 50. Two particulate (soot) filters 52 and 54 of known design trap the particulates. The filters 52 and 54 may be sequentially or simultaneously regenerated to generate carbon monoxide. The carbon monoxide, a reducing agent, is introduced into the exhaust stream. One filter may be lighted off so as to be regenerated and produce CO while the other continues to operate. Logic and sensory means may be used to selectively control the filters 52 and 54.

The filtered exhaust stream, augmented by the CO or alternatively by other reducing agents (urea, fuel, hexane etc.) from source 56, flows into the second zone 58. The second zone 58 includes the catalytic foam substrate 60 as discussed herein.

After the gases are "denoxed" (that is, treated to remove NO_x), the stream is then routed through a third zone 62 housing an oxidizing catalyst 64. The catalyst 64, generally made from platinum, will treat and substantially remove most of the remaining CO.

The treated gas, sans NO_x , CO and hydrocarbons, is routed to a muffler (not shown) and then out to the atmosphere.

The instant invention provides a method for the reduction of nitrogen oxides present in exhaust gases, particularly diesel exhausts.

In general, the exhaust stream is contacted with a catalyst comprising a metal or alloy including the metals of Groups I-B and VIII, supported on a sponge-like metallic substrate in the presence of sufficient reducing agent within a temperature range of 200°C to 600°C. It is preferred to utilize a plated nickel foam substrate made in accordance with U.S. Patent 5,195,716.

In essence, in order to produce the catalyst nickel carbonyl is decomposed so as to deposit metallic nickel onto a polymeric foam. The nickel plates out within the interstices of the foam to form a nickel coated foam or sponge. The carbonyl plating process is amenable to laying down other metals onto the substrate.

The resulting nickel foam has a huge internal surface area capable of holding the subsequently plated catalytic material. It may be appreciated that the gases flowing within the foam will course through tortuous paths. This action permits repeated contacts between the gases and the catalyst.

In a more specific embodiment of the present invention, there is provided a method for treating diesel exhaust gases in a multiple zone system operating at a preferred temperature of about 400°C. In zone one 50, particulates are filtered and removed from the exhaust gases. Commercially available carbon particulate traps cleanse the stream. In zone two 58, as the gases pass over a metallic silver catalyst supported by the metallic nickel sponge, carbon monoxide or some other reducing agent introduced into the stream, catalytically reduces the NO_x to N_2 and CO_2 . The CO may be generated in a conventional manner such as lighting off and then regenerating a spent filter of zone one 50. Any CO escaping from zone two is oxidized in zone three 62 when it is contacted with an oxidizing catalyst, i.e., platinum.

As an alternative to the CO, a hydrocarbon fuel, introduced into the exhaust upstream, was equally ef-

fective in reducing NO_x levels.

Any one of the known catalytic actors may be deposited on the nickel foam substrate. However, to test the efficacy of the invention metallic silver was used.

The silver catalyst was prepared by electroplating the nickel sponge from a cyanide bath (minus the brighteners) as described in the U.S. Patent No. 2,666,738. The procedure calls for one to two microns of silver deposit. A current density of 50 amperes per m² (0.5 ampere per dm²) applied to the nickel sponge having a surface area 0.8 dm²/g, immersed in an electrolyte containing 45 g/l silver cyanide (AgCN), 115 g/l potassium cyanide (KCN), and 22 g/l potassium carbonate (K₂CO₃), has a deposition rate of about 0.319 dm⁻¹s⁻¹ at a room temperature of 22°C. The deposit was then annealed in a nitrogen atmosphere at 800°C for approximately 30 minutes.

Example 1

In this example, the reduction of NO (nitric oxide) to N₂ was accomplished with the apparatus depicted in Figure 1 by passing a synthetic diesel exhaust gas containing 4.2% CO₂, 5.8% O₂, 6.3% H₂O, 27 ppm CO and 3700 ppm NO with N₂ accounting for the remainder over a silver coated nickel sponge. The catalyst was contained in a steel tube 16 positioned within the furnace 14. The silver catalyst was characterized by a surface area of about 0.4 m²/g and an average pore diameter of approximately 600 microns. NO conversions were for exhaust gases with space velocities of about 20,000 and 32,000 volume/volume/hour (v./v./h) at 400°C by collection and high pressure liquid chromatography (HPLC) analysis on scrub solutions from the effluent gases.

Four test runs were conducted. Run 1 was a calibration run. Run 2 was run through the reactor 12 without hexane. Note that no NO reduction occurred. In tests 3 and 4, NO conversion was accomplished. 0.37% (3700 ppm) of hexane (C₆H₁₄) was introduced to the synthetic exhaust described above. Table 1 shows that the catalyst described herein is effective for conversion of NO contained in exhaust gases at a temperature of about 400°C.

Table 1

Run	Cat. Temp. (°C)	Space Vel. (v./v./h)	Hexane	NO Conversion after 30 Minutes Operation
1	22*	20,000	0.0	0.0
2	415**	20,000	0.0	0.0
3	422	20,000	0.15	0.0
4	422	32,000	0.37	53.6

*By-Pass run. The exhaust gases were routed through line 30 to calibrate the analyzer 34.

**Blank run. The exhaust gases were routed through the reactor 14 without a reducing agent.

Example 2

In another series of tests, effective reduction of NO to N₂ was accomplished by passing a synthetic diesel exhaust gas containing 3.7% CO₂, 8.0% O₂, 7.9% H₂O, 0.52% CO, 0.52% & 0.78% NO (CO= NO & 1.5 x NO), with the remainder being N₂, through the silver nickel foam catalyst 16 at 400°C with and without the introduction of additional carbon monoxide. Table 2 shows that the catalyst described herein is effective in the conversion of NO contained in exhaust gases at about 400°C. Carbon monoxide was added in a 1:1 and 1:1.5 ratio of NO:CO. NO reduction appeared to be just as effective as it was with hexane (fuel) as a reducing agent.

Table 2

Cat. Temp. (°C)	Space Vel. (v.v ⁻¹ h ⁻¹)	CO added (%)	NO Conversion After 30 minute operation (%)
22*	19,500	0.0	0.0
423**	19,500	0.0	0.0
374	24,000	0.52	53.1
393	25,000	0.73	61.7

*By -Pass run. The exhaust gases were routed through line 30 to calibrate the analyzer 34.

**Blank run. The exhaust gases were routed through the reactor 14 without a reducing agent.

While in accordance with the provisions of the statute, there is illustrated and described herein specific embodiments of the invention, those skilled in the art will understand that changes may be made in the form of the invention covered by the claims and that certain features of the invention may sometimes be used to advantage without a corresponding use of the other features.

Claims

1. A catalytic converter for treating exhaust gases, the converter comprising a reactor (12), a metal foam substrate (16) disposed within the reactor, catalytic material attached to the substrate, and means for supplying a reducing agent (52,54) to the exhaust gases, the reducing agent preferably being selected from the group consisting of carbon monoxide, urea, ammonia and hydrocarbon fuels.
2. The converter according to claim 1 wherein the substrate (16) includes nickel plated polymeric foam.
3. The converter according to claim 1 or claim 2, wherein the catalytic material is selected from the group consisting of the Group I-B and VIII elements, e.g. silver.
4. The converter according to any one of claims 1 to 3, including a first particulate filter (52,54), a second NO_x treatment catalyst (12) housing the catalytic material and the substrate (16), and a third oxidizing catalyst (64).
5. A process for reducing the nitrogen oxide content of an exhaust gas stream generated by an internal combustion engine, the process comprising:
 - (a) contacting the stream with a catalyst supported on a metal foam substrate (16), which preferably includes nickel,
 - (b) introducing a reducing agent into the exhaust gas stream, and
 - (c) maintaining the process temperature between about 200°C to about 600°C.
6. The process according to claim 5, wherein the catalyst is selected from a group consisting of the Group I-B and VIII elements, e.g. silver.
7. The process according to claim 5 or claim 6, wherein the reducing agent is selected from the group con-

sisting of hydrocarbon fuels, carbon monoxide, urea and ammonia.

8. The process according to any one of claims 5 to 7 wherein the exhaust gas stream is contacted with a catalyst including silver deposited on a nickel foam structure (16), in the presence of carbon monoxide, and at a temperature range between about 200°C to about 600°C.
9. A process for the treatment of diesel engine exhaust gases, the process including contacting the gas with a silver catalyst deposited on a nickel foam substrate (16) in the presence of a reducing agent at a temperature of about 200°C to about 600°C and removing at least a portion of the nitrogen oxides in the gases.
10. The process according to claim 9, where the gases are first routed to a particulate filter (52,54), then are brought into contact with the silver catalyst, and then are brought into contact with an oxidizing catalyst.

FIG. 1

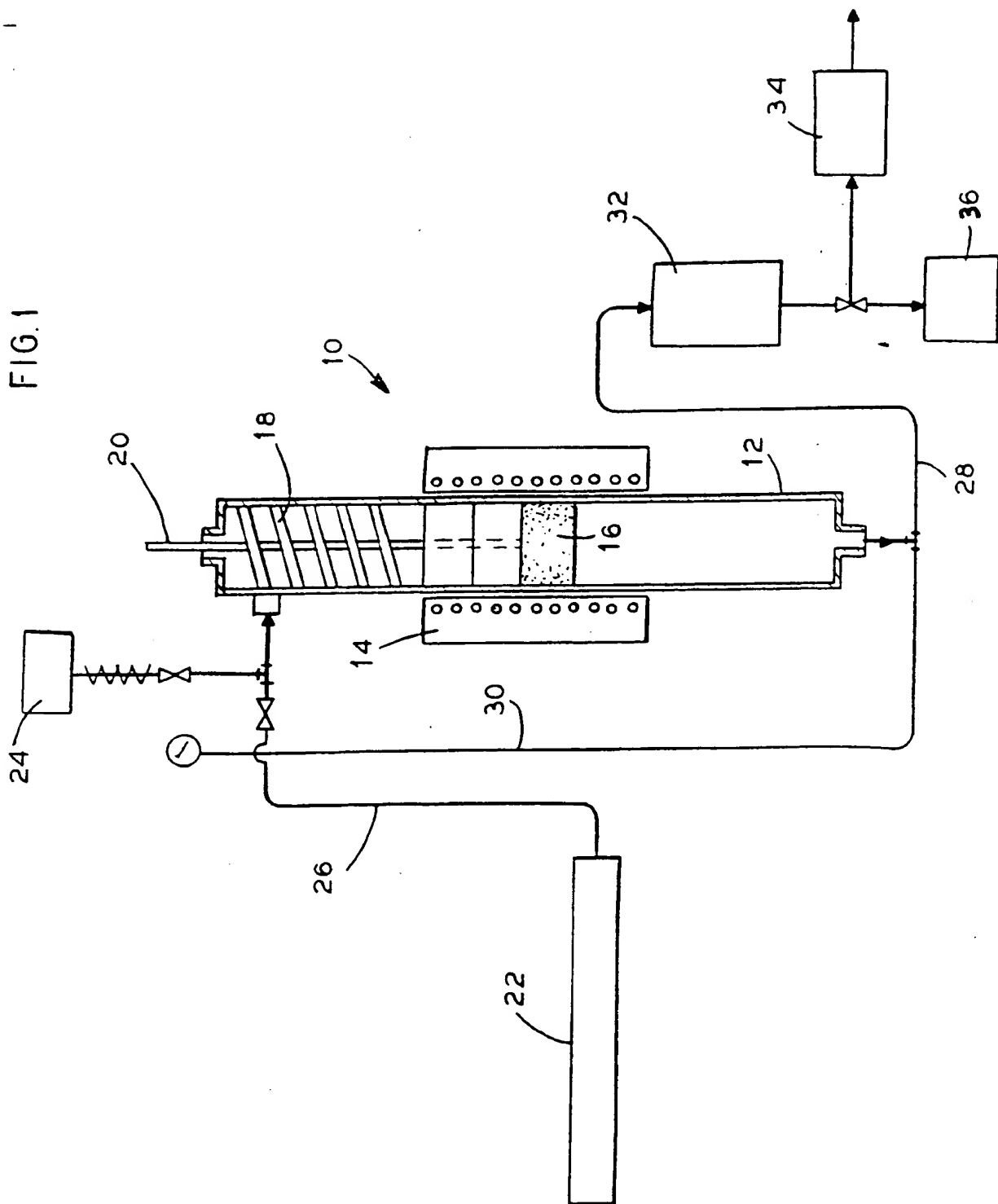
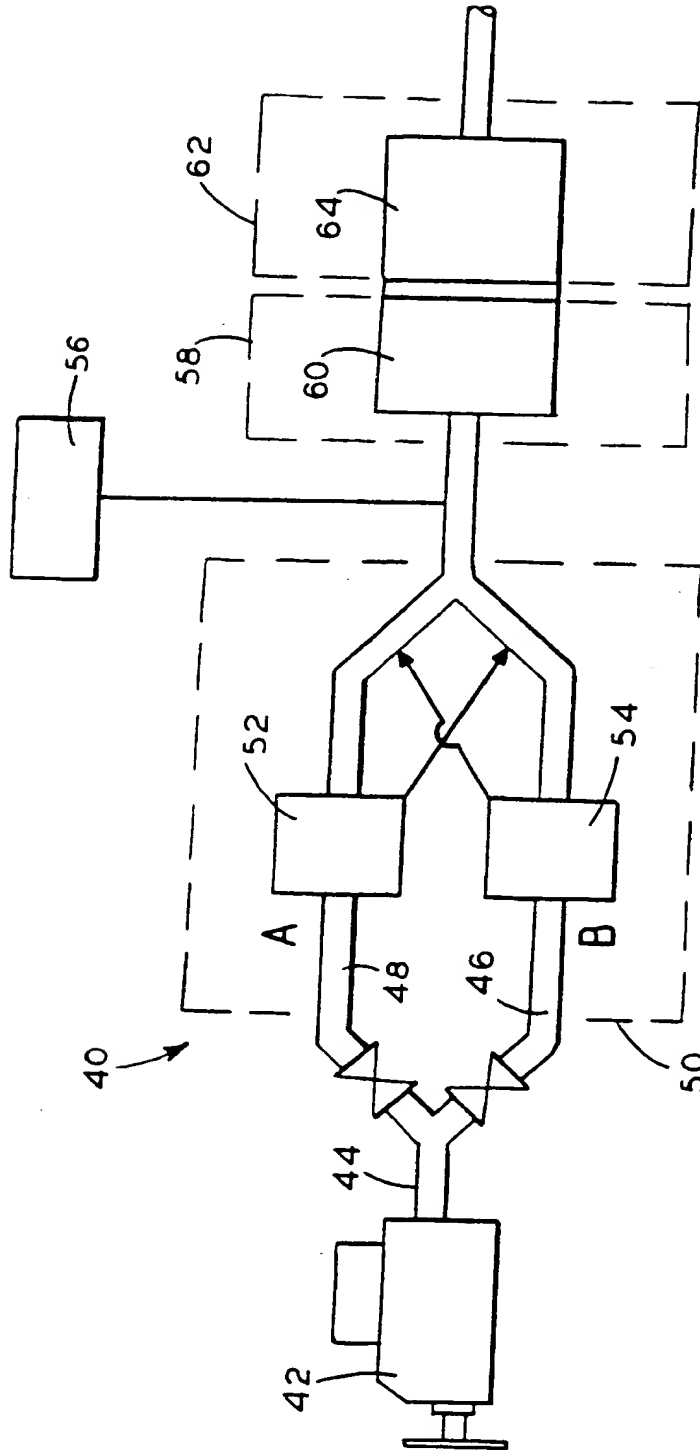


FIG. 2





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EUROPEAN PATENT APPLICATION

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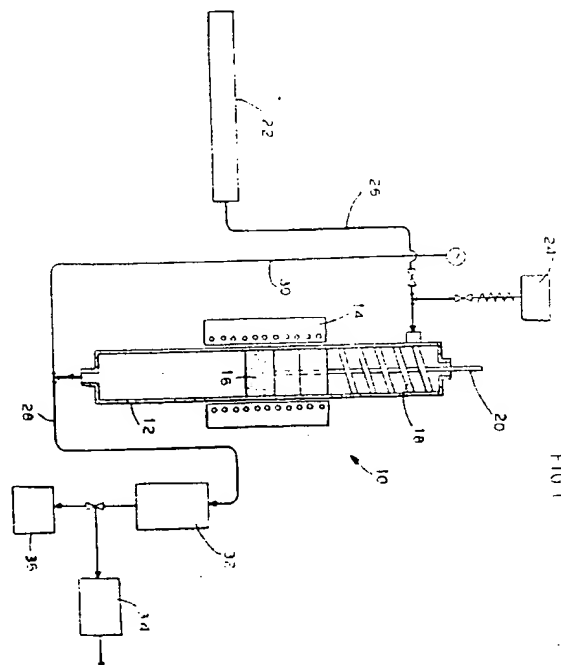
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54 **Catalytic conversion of internal combustion engine exhaust gases.**

57 A catalytic converter for treating exhaust gases, the converter comprising a reactor (12), a metal foam substrate (12) disposed within the reactor (12) wherein the substrate (16) includes nickel plated polymeric foam, catalytic material attached to the substrate (e.g. silver) and means (56) for supplying a reducing agent to the exhaust gases, the reducing agent being selected from the group consisting of carbon monoxide, urea, ammonia and hydrocarbon fuels. The process temperature is maintained between 200°C and 600°C.



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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 4082

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	DATABASE WPI Section Ch, Week 7803, 1978 Derwent Publications Ltd., London, GB; Class E31, AN 78-05017A & JP-A-52 142 662 (MITSUBISHI) 28 November 1977	1	F01N3/10 F01N3/28 B01D53/36
Y	* abstract * ---	2-5,7	
Y	DATABASE WPI Section Ch, Week 8208, 1982 Derwent Publications Ltd., London, GB; Class H06, AN 82-15003E & JP-A-57 010 319 (TOYOTA) 19 January 1982 * abstract *	2,3	
Y	PATENT ABSTRACTS OF JAPAN vol. 7, no. 14 (C-146) 20 January 1983 & JP-A-57 171 425 (MITSUBISHI) 22 October 1982 * abstract *	4,5,7	
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 239 (M-1258) 2 June 1992 & JP-A-04 050 421 (HINO) 19 February 1992 * abstract *	4	TECHNICAL FIELDS SEARCHED (Int.Cl.5) F01N
A	EP-A-0 198 435 (BASF) * column 4, line 15 - column 5, line 27; figure 1 *	2	
A	FR-A-2 393 145 (CATERPILLAR) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31 October 1994	Examiner Sideris, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

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